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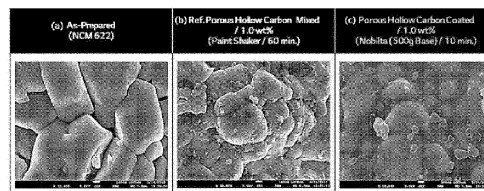
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(54) **METHOD FOR PRODUCING POSITIVE ELECTRODE ACTIVE MATERIAL FOR LITHIUM SECONDARY BATTERY, AND POSITIVE ELECTRODE ACTIVE MATERIAL PRODUCED THEREBY FOR LITHIUM SECONDARY BATTERY**

(57) The present invention relates to a method for producing a positive electrode active material, a positive electrode active material produced by the method, thereby having a BET specific surface area of 10 m<sup>2</sup>/g or less, a positive electrode including the positive electrode active material, and a lithium secondary battery, wherein the method includes preparing a lithium transition metal oxide in the form of a secondary particle in which primary particles are aggregated, mixing the lithium transition metal oxide and a carbon-based material of a hollow structure having a plurality of pores to form a mixture, and surface treating the mixture in a mechanical manner to form a carbon coating layer on the surface of the lithium transition metal oxide, wherein the carbon-based material of a hollow structure having a plurality of pores has a specific surface area of 200 m<sup>2</sup>/g or greater and a graphitization degree(I<sub>D</sub>/I<sub>G</sub>) of 0.5 or greater.

[FIG. 2]



**Description****TECHNICAL FIELD****Cross-reference to Related Applications**

[0001] This application claims the benefit of Korean Patent Application No. 10-2019-0127314, filed on October 14, 2019, in the Korean Intellectual Property Office, the disclosure of which is incorporated herein in its entirety by reference.

**Technical Field**

[0002] The present invention relates to a method for producing positive electrode active material for a lithium secondary battery, a positive electrode active material produced by the production method, a positive electrode for a lithium secondary battery including the positive electrode active material, and a lithium secondary battery.

**BACKGROUND ART**

[0003] As technology development and demand for mobile devices have increased, the demand for secondary batteries as an energy source has been rapidly increased. Among such secondary batteries, lithium secondary batteries having high energy density and voltage, long cycle life, and low self-discharging rate have been commercialized and widely used.

[0004] As a positive electrode active material of a lithium secondary battery, a lithium transition metal oxide is used. Among such lithium transition metal oxides, a lithium-cobalt oxide, such as  $\text{LiCoO}_2$ , which has a high functional voltage and excellent capacity properties has been mainly used. However,  $\text{LiCoO}_2$  has very poor in thermal properties due to the destabilization of a crystal structure according to de-lithium, and is also expensive. Therefore,  $\text{LiCoO}_2$  has a limitation in being used as a power source in a field such as an electric vehicle or the like in a large amount.

[0005] As a material to replace  $\text{LiCoO}_2$ , a lithium-manganese composite metal oxide ( $\text{LiMnO}_2$ ,  $\text{LiMn}_2\text{O}_4$ , or the like), a Lithium iron phosphate compound ( $\text{LiFePO}_4$ , or the like), a lithium-nickel composite metal oxide (  $\text{LiNiO}_2$ , or the like), and the like have been developed. Among the above materials, research and development has been actively conducted on a lithium nickel composite metal oxide which has a high reversible capacity of about 200 mAh/g, thereby easily implementing a high capacity battery. However, when compared with  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$  has a lower thermal stability, and has a problem in that when an internal short circuit occurs due to external pressure or the like in a charged state, a positive electrode active material itself is decomposed, causing the rupture and ignition of a battery. Accordingly, as a method for improving the thermal stability of  $\text{LiNiO}_2$ , which is low, while maintaining the excellent reversible capacity thereof,  $\text{LiNi}_{1-\alpha}\text{Co}_\alpha\text{O}_2$  ( $\alpha=0.1\sim0.3$ ), in which a part of nickel is substituted with cobalt, or a lithium-nickel-cobalt metal oxide, in which a part of nickel is substituted with Mn, Co, or Al, has been developed.

[0006] However, as for the lithium-nickel-cobalt metal oxide, due to the sharp increase in cobalt price, Co-less positive electrode material not containing cobalt, or Ni-rich positive electrode material containing Ni in excess has been actively studied in terms of cost and energy density.

[0007] Meanwhile, compared to a Co-rich composition which has been typically used and in which cobalt is used in excess, the Co-less positive electrode material or the Ni-rich positive electrode material has a problem of having low electrical conductivity of positive electrode active material and being vulnerable to moisture. In order to solve the above problem, there has been an attempt to form a carbon coating layer on the surface of the above-described positive electrode material using a pitch and the like. However, in the case of a carbon coating layer, there is a disadvantage in that a high-temperature heat treatment for carbonization should be accompanied, and when the high-temperature heat treatment is performed, a carbon element on a surface reacts with oxygen on the surface of a positive electrode material and reduced, which causes the oxidation number of the positive electrode material to greatly change, resulting in deteriorating the performance of the positive electrode material.

[0008] Therefore, there has been a demand for developing a positive electrode active material that can improve electrical conductivity and lifespan properties by forming a thin and uniform carbon coating layer on the surface of the positive electrode active material without the change in the oxidation number of the surface of a positive electrode material caused by a high-temperature heat treatment process.

**DISCLOSURE OF THE INVENTION****TECHNICAL PROBLEM**

[0009] In order to solve the above problem, the first aspect of the present invention provides a method for producing a positive electrode active material, the method in which a lithium transition metal oxide is surface-treated in a mechanical

manner with a carbon-based material of a hollow structure, so that a uniform carbon coating layer is formed on the surface thereof.

[0010] The second aspect of the present invention provides a positive electrode active material with improved conductivity by having a carbon coating layer formed on the surface thereof and having a low BET specific surface area of 10 m<sup>2</sup>/g or less.

[0011] The third aspect of the present invention provides a positive electrode for a lithium secondary battery including the positive electrode active material.

[0012] The fourth aspect of the present invention provides a lithium secondary battery including the positive electrode.

## TECHNICAL SOLUTION

[0013] According to an aspect of the present invention, there is provided a method for producing a positive electrode active material, wherein the method includes preparing a lithium transition metal oxide in the form of a secondary particle in which primary particles are aggregated, mixing the lithium transition metal oxide and a carbon-based material of a hollow structure having a plurality of pores to form a mixture, and surface treating the mixture in a mechanical manner to form a carbon coating layer on the surface of the lithium transition metal oxide, wherein the carbon-based material of a hollow structure having a plurality of pores has a specific surface area of 200 m<sup>2</sup>/g or greater and a graphitization degree( $I_D/I_G$ ) of 0.5 or greater.

[0014] According to another aspect of the present invention, there is provided a positive electrode active material including a lithium transition metal oxide in the form of a secondary particle in which primary particles are aggregated, and a carbon coating layer formed on the surface of the lithium transition metal oxide, wherein the carbon coating layer is formed on the surface of the primary particle and the surface of the secondary particle of the lithium transition metal oxide, and has a BET specific surface area of 10 m<sup>2</sup>/g or less.

[0015] According to another aspect of the present invention, there is provided a positive electrode for a lithium secondary battery including the positive electrode active material.

[0016] According to another aspect of the present invention, there is provided a lithium secondary battery including the positive electrode for a lithium secondary battery.

## ADVANTAGEOUS EFFECTS

[0017] According to the present invention, a positive electrode active material that can improve electrical conductivity and lifespan properties may be provided since there is no change in the oxidation number of the surface of a positive electrode material and a thin and uniform carbon coating layer is formed by not performing a high-temperature heat treatment when forming a carbon coating layer on the surface of a lithium transition metal oxide.

## BRIEF DESCRIPTION OF THE DRAWINGS

[0018]

(a) of FIG. 1 is a TEM image of a hollow carbon-based material having a plurality of pores and used in Examples of the present invention, and (b) of FIG. 1 is an SEM image showing a carbon-based material having a dense structure and used in Comparative Examples 3 to 4;

FIG. 2 is SEM images showing (a) a positive electrode active material of Comparative Example 2, (b) a positive electrode active material of Comparative Example 1, and (c) a positive electrode active material of Example 1;

FIG. 3 is SEM images showing (a) a positive electrode active material of Comparative Example 2, (b) a positive electrode active material of Comparative Example 4, and (c) a positive electrode active material of Example 1;

FIG. 4 is SEM images showing (a) a positive electrode active material of Comparative Example 2, (b) a positive electrode active material of Example 2, and (c) a positive electrode active material of Example 1; and

FIG. 5 is SEM images and energy dispersive X-ray (EDX) images of (a) a positive electrode active material of Example 2, (b) a positive electrode active material of Comparative Example 3.

## BEST MODE FOR CARRYING OUT THE INVENTION

[0019] Hereinafter, the present invention will be described in more detail.

[0020] It will be understood that words or terms used in the specification and claims of the present invention shall not be construed as being limited to having the meaning defined in commonly used dictionaries. It will be further understood that the words or terms should be interpreted as having meanings that are consistent with their meanings in the context of the relevant art and the technical idea of the invention, based on the principle that an inventor may properly define

the meaning of the words or terms to best explain the invention.

**[0021]** In the entire present specification, a "specific surface area" is measured by a BET method, and specifically, may be calculated from the adsorption amount of nitrogen gas under a liquid nitrogen temperature (77K) using Belsorp-mino II of BEL Japan Co., Ltd.

**[0022]** In the entire present specification, a "graphitization degree" means a degree to which amorphous carbon changes partially or entirely into crystalline graphite, and may be confirmed using Raman spectroscopy. The structure of a carbon-based material may be analyzed thereby. In the Raman spectrum of a carbon-based material, a G-band is a peak indicating an  $sp^2$  bond of the carbon-based material, and it indicates a carbon crystal with no structural defects. A D-band is a peak indicating an  $sp^3$  bond of the carbon-based material, and it increases when an atomic bond formed by the  $sp^2$  bond is broken and becomes the  $sp^3$  bond. The above D band increases when disorders or defects present in the carbon-based material are generated, so that it is possible to quantitatively evaluate the degree of disorder or defect generation by calculating the ratio ( $I_D/I_G$ ) of the maximum peak intensity ( $I_D$ ) of the D band to the maximum peak intensity ( $I_G$ ) of the G band.

**[0023]** In the entire present specification, a 'primary particle' means a primary structural body of a single particle, and a 'secondary particle' means an aggregate in which primary particles are aggregated by physical or chemical bonding between the primary particles without an intentional aggregation or assembly process for primary particles constituting a secondary particle, that is, a secondary structural body.

#### Method for preparing positive electrode active material

**[0024]** The present inventors have found that, when forming a carbon-based coating layer on a lithium transition metal oxide, if a carbon-based material having a specific structure is used and the carbon-based coating layer is formed by a mechanofusion method at this time, a uniform and thin carbon coating layer may be formed on the surface thereof without the change in the structure of the lithium transition metal oxide, and have completed the present invention.

**[0025]** Specifically, a method for producing a positive electrode active material according to the present invention includes preparing a lithium transition metal oxide in the form of a secondary particle in which primary particles are aggregated, mixing the lithium transition metal oxide and a carbon-based material of a hollow structure having a plurality of pores to form a mixture, and surface treating the mixture in a mechanical manner to form a carbon coating layer on the surface of the lithium transition metal oxide, wherein the carbon-based material of a hollow structure having a plurality of pores has a specific surface area of 200  $m^2/g$  or greater and a graphitization degree ( $I_D/I_G$ ) of 0.5 or greater.

**[0026]** Hereinafter, the method for producing a positive electrode active material according to the present invention will be described in more detail.

**[0027]** First, in order to produce a positive electrode active material according to the present invention, a lithium transition metal oxide in the form of a secondary particle in which primary particles are aggregated is prepared.

**[0028]** For example, the lithium transition metal oxide may be a secondary particle formed by the aggregation of primary particles having a crystal grain of 10 nm to 5,000 nm, preferably 10 nm to 3,000 nm. Since the lithium transition metal oxide is formed as a secondary particle in which primary particles are aggregated, the energy density per volume of an electrode may be increased.

**[0029]** In addition, since the lithium transition metal oxide is formed in the form of a secondary particle in which primary particles are aggregated, the contact area between the lithium transition metal oxide and an electrolyte solution is large, and the travel distance of lithium ions in the lithium transition metal oxide is short, so that high capacity and high power properties may be easily exhibited.

**[0030]** Next, a mixture is formed by mixing the lithium transition metal oxide and a carbon-based material of a hollow structure having a plurality of pores.

**[0031]** According to the present invention, the carbon-based material of a hollow structure having a plurality of pores may have a specific surface area of 200  $m^2/g$  or greater, preferably 200  $m^2/g$  to less than 500  $m^2/g$ , more preferably 200  $m^2/g$  to 400  $m^2/g$ , and at this time, the graphitization degree ( $I_D/I_G$ ) thereof is 0.5 or greater. Preferably 0.5 to 2.0, most preferably 1.0 to 2.0.

**[0032]** As shown in (a) of FIG. 1, the carbon-based material of a hollow structure according to the present invention has a form in which particles having low crystallinity are aggregated. In this case, since structural collapse easily occurs by force applied from the outside, when a carbon coating layer is formed using the same, the carbon-based material is crushed and brought into close contact with the surface of the lithium transition metal oxide due to the structural collapse of the carbon-based material by force applied from the outside, so that a carbon coating layer may be formed to a uniform thickness on the surface of a secondary particle, and in particular, the carbon coating layer may be uniformly formed even at the boundary between primary particles. As a result, the conductivity of the positive electrode active material may be improved, and the BET specific surface area thereof may also be maintained low, so that side reactions and the like with an electrolyte solution due to an increase in the BET specific surface area may be prevented in advance.

**[0033]** For example, as shown in (b) of FIG. 1, the carbon-based material of a hollow structure according to the present

invention has a form in which primary particles are aggregated to each other, wherein the primary particles have a dense structure in which the inside of a particle is filled with carbon tissues, and as a result, structural collapse does not occur. Therefore, even if force is applied from the outside, the structural collapse of the carbon-based material does not occur and the carbon-based material may be coated on the lithium transition metal oxide while maintaining crystallinity, so that the BET specific surface area may increase. In addition, since the carbon-based material forms a carbon-based coating layer without the structural collapse thereof in the form of sticking to the surface of the lithium transition metal oxide, a carbon coating layer is not easily formed at the boundary between primary particles, so that it is not easy to form a uniform carbon coating layer.

**[0034]** As for the lithium transition metal oxide and the carbon-based material, the carbon-based material may be mixed in an amount of 0.1 to 2 parts by weight, preferably 0.1 to 1 part by weight based on 100 parts by weight of the lithium transition metal oxide. For example, when the carbon-based material is mixed in the above-described range, a uniform carbon coating layer may be formed at the boundary surface between primary particles of the lithium transition metal oxide as well as on the entire surface of the lithium transition metal oxide. On the other hand, when the carbon-based material exceeds 2 parts by weight based on 100 parts by weight of the lithium transition metal oxide, an excessively thick carbon-based coating layer is formed. Therefore, the carbon-based coating layer may rather hinder the diffusion of lithium ions, so that the input/output properties of a battery may be deteriorated.

**[0035]** Next, a carbon coating layer is formed on the surface of the lithium transition metal oxide by surface treating the mixture in a mechanical manner.

**[0036]** The surface treating of the mixture in a mechanical manner according to the present invention may be performed by a mechanofusion method. Specifically, the mechanofusion method may be performed using a nobilta device under a dry process condition in which an additive such as a solvent, a binder, and the like is not additionally included. Specifically, the mechanofusion method may be performed while stirring a reactor at room temperature (20°C) with a current of 3 to 15 A, a power of 0.2 to 5.5 W, and a rotational speed of 500 to 6,000 rpm based on a 0.5 L nobilta device. The mechanofusion method may have different current, power, rotational speed conditions depending on the capacity of a device. For example, if the capacity of a device is increased, power may be increased but a rotational speed may be decreased. Specifically, for example, when a nobilta device of 300 L capacity is used, the mechanofusion method may be performed while stirring at a rotational speed of 50 to 800 rpm at a power of 10 to 200 W. Since the dispersibility of particles is improved by the above-described mechanofusion method, a carbon material may be separated at uniform intervals on the surface of a lithium transition metal oxide to form a carbon coating layer at the boundary between primary particles as well as on the surface of a secondary particle.

#### **Positive electrode active material**

**[0037]** In addition, the present invention provides a positive electrode active material produced by the above-described method, wherein the positive electrode active material includes a lithium transition metal oxide in the form of a secondary particle in which primary particles are aggregated, and a carbon coating layer formed on the surface of the lithium transition metal oxide. The carbon coating layer is formed on the surface of the primary particle and the surface of the secondary particle of the lithium transition metal oxide, and the carbon coating layer has a thickness of 500 nm or less, preferably 5 nm to 100 nm, and has a BET specific surface area of 10 m<sup>2</sup>/g or less.

**[0038]** Preferably, the positive electrode active material according to the present invention has a BET specific surface area of 1.0 m<sup>2</sup>/g to 10 m<sup>2</sup>/g, preferably 1.0 m<sup>2</sup>/g to 6.0 m<sup>2</sup>/g, more preferably 1.0 m<sup>2</sup>/g to 3.0 m<sup>2</sup>/g. When the BET specific surface area is in the above-described range, the change in specific surface area due to the formation of a carbon coating layer is minimized, so that side reactions between a positive electrode active material and an electrolyte solution may be suppressed.

**[0039]** In addition, the positive electrode active material according to the present invention has a powder electrical conductivity of  $2.7 \times 10^{-3}$  S/cm to  $10.0 \times 10^{-3}$  S/cm, preferably  $4.0 \times 10^{-3}$  S/cm to  $10.0 \times 10^{-3}$  S/cm, which is measured after pressing the same by applying a force of 5 kN to 20 kN, preferably 10 to 20 kN, most preferably 20 kN thereto. As described above, since the electrical conductivity of the positive electrode active material itself greatly increases due to the formation of the carbon coating layer on the surface, when the positive electrode active material is applied to a battery, the electrochemical properties of the battery, such as input and output properties, lifespan properties, and the like, may be improved.

#### **Positive electrode**

**[0040]** In addition, the present invention provides a positive electrode for a lithium secondary battery, the positive electrode including a positive electrode active material prepared by the method described above.

**[0041]** Specifically, the positive electrode includes a positive electrode current collector and a positive electrode active material layer formed on at least one surface of the positive electrode current collector and including the above-described

positive electrode active material.

[0042] The positive electrode current collector is not particularly limited as long as it has conductivity without causing a chemical change in a battery. For example, stainless steel, aluminum, nickel, titanium, fired carbon, or aluminum or stainless steel that is surface-treated with one of carbon, nickel, titanium, silver, and the like may be used. Also, the positive electrode current collector may typically have a thickness of 3 to 500  $\mu\text{m}$ , and microscopic irregularities may be formed on the surface of the current collector to improve the adhesion of a positive electrode active material. For example, the positive electrode current collector may be used in various forms such as a film, a sheet, a foil, a net, a porous body, a foam, and a non-woven body.

[0043] The positive electrode active material layer may include a conductive material and a binder, together with a positive electrode active material.

[0044] At this time, the positive electrode active material may be included in an amount of 80 to 99 wt%, more specifically 85 to 98 wt% based on the total weight of the positive electrode active material layer. When included in the above content range, excellent capacity properties may be exhibited.

[0045] At this time, the conductive material is used to impart conductivity to an electrode, and any conductive material may be used without particular limitation as long as it has electron conductivity without causing a chemical change in a battery to be constituted. Specific examples thereof may include graphite such as natural graphite or artificial graphite; a carbon-based material such as carbon black, acetylene black, Ketjen black, channel black, furnace black, lamp black, thermal black, and carbon fiber; metal powder or metal fiber of such as copper, nickel, aluminum, and silver; a conductive whisker such as a zinc oxide whisker and a potassium titanate whisker; a conductive metal oxide such as a titanium oxide; or a conductive polymer such as a polyphenylene derivative, and any one thereof or a mixture of two or more thereof may be used. The conductive material may be included in an amount of 1 to 30 wt% based on the total weight of the positive electrode active material layer.

[0046] The binder serves to improve the bonding between positive electrode active material particles and the adhesion between the positive electrode active material and the current collector. Specific examples thereof may include polyvinylidene fluoride (PVDF), a polyvinylidene fluoride-hexafluoropropylene copolymer (PVDF-co-HFP), polyvinyl alcohol, polyacrylonitrile, carboxymethyl cellulose (CMC), starch, hydroxypropyl cellulose, regenerated cellulose, polyvinylpyrrolidone, polytetrafluoroethylene, polyethylene, polypropylene, an ethylene-propylene-diene monomer (EPDM), a sulfonated EPDM, styrene-butadiene rubber (SBR), fluorine rubber, or various copolymers thereof, and any one thereof or a mixture of two or more thereof may be used. The binder may be included in an amount of 1 to 30 wt% based on the total weight of the positive electrode active material layer.

[0047] The positive electrode may be manufactured according to a typical method for manufacturing a positive electrode except that the positive electrode active material described above is used. Specifically, the positive electrode may be manufactured by applying a composition for forming a positive electrode active material layer, which is prepared by dissolving or dispersing the positive electrode active material described above and selectively, a binder and a conductive material in a solvent, on a positive electrode current collector, followed by drying and pressing. At this time, the type and content of the positive electrode active material, the binder, and the conductive material are as described above.

[0048] The solvent may be a solvent commonly used in the art, and may be dimethyl sulfoxide (DMSO), isopropyl alcohol, N-methylpyrrolidone (NMP), acetone, water, or the like. Any one thereof or a mixture of two or more thereof may be used. The amount of the solvent to be used is sufficient if the solvent may dissolve and disperse the positive electrode active material, the binder, and the conductive material in consideration of the applying thickness of a slurry and preparation yield, and thereafter, have a viscosity which may exhibit excellent thickness uniformity during application for manufacturing a positive electrode.

[0049] In addition, in another method, the positive electrode may be manufactured by casting the composition for forming a positive electrode active material layer on a separate support and then laminating a film obtained by being peeled off from the support on a positive electrode current collector.

### **Lithium secondary battery**

[0050] In addition, the present invention may manufacture an electrochemical device including the positive electrode. The electrochemical device may be specifically a battery, a capacitor, or the like, and more specifically, may be a lithium secondary battery.

[0051] Specifically, the lithium secondary battery includes a positive electrode, a negative electrode positioned to face the positive electrode, a separator interposed between the positive electrode and the negative electrode, and an electrolyte. The positive electrode is the same as that described above, and thus, a detailed description thereof will be omitted. Hereinafter, only the rest of the components will be described in detail.

[0052] Also, the lithium secondary battery may selectively further include a battery case for accommodating an electrode assembly composed of the positive electrode, the negative electrode, and the separator, and a sealing member for sealing the battery case.

**[0053]** In the lithium secondary battery, the negative electrode includes a negative electrode current collector and a negative electrode active material layer positioned on the negative electrode current collector.

**[0054]** The negative electrode current collector is not particularly limited as long as it has a high conductivity without causing a chemical change in a battery. For example, copper, stainless steel, aluminum, nickel, titanium, fired carbon, copper or stainless steel that is surface-treated with one of carbon, nickel, titanium, silver, and the like, an aluminum-cadmium alloy, and the like may be used. Also, the negative electrode current collector may typically have a thickness of 3  $\mu\text{m}$  to 500  $\mu\text{m}$ , and as in the case of the positive electrode current collector, microscopic irregularities may be formed on the surface of the negative electrode current collector to improve the adhesion of a negative electrode active material. For example, the negative electrode current collector may be used in various forms such as a film, a sheet, a foil, a net, a porous body, a foam, and a non-woven body.

**[0055]** The negative electrode active material layer selectively includes a binder and a conductive material in addition to a negative electrode active material.

**[0056]** As the negative electrode active material, a compound capable of reversible intercalation and de-intercalation of lithium may be used. Specific examples thereof may include a carbonaceous material such as artificial graphite, natural graphite, graphitized carbon fiber, and amorphous carbon; a (semi)metal-based material alloyable with lithium such as Si, Al, Sn, Pb, Zn, Bi, In, Mg, Ga, Cd, an Si alloy, an Sn alloy, or an Al alloy; a (semi)metal oxide which may be doped and undoped with lithium such as SiOp ( $0 < \beta < 2$ ), SnO<sub>2</sub>, a vanadium oxide, and a lithium vanadium oxide; or a composite including the (semi)metal-based material and the carbonaceous material such as an Si-C composite or an Sn-C composite, and any one thereof or a mixture of two or more thereof may be used. Also, a metal lithium thin film may be used as the negative electrode active material. Furthermore, low crystalline carbon, high crystalline carbon and the like may all be used as a carbon material. Representative examples of the low crystalline carbon may include soft carbon and hard carbon, and representative examples of the high crystalline carbon may include irregular, planar, flaky, spherical, or fibrous natural graphite or artificial graphite, Kish graphite, pyrolytic carbon, mesophase pitch-based carbon fiber, meso-carbon microbeads, mesophase pitches, and high-temperature sintered carbon such as petroleum or coal tar pitch derived cokes.

**[0057]** The negative electrode active material may be included in an amount of 80 parts by weight to 99 parts by weight based on a total weight of 100 part by weight of a negative electrode active material layer.

**[0058]** The binder is a component for assisting in bonding between a conductive material, an active material, and a current collector, and is typically added in an amount of 0.1 parts by weight to 10 parts by weight based on a total weight of 100 parts by weight of a negative electrode active material layer. Examples of the binder may include polyvinylidene fluoride (PVDF), polyvinyl alcohol, carboxymethyl cellulose (CMC), starch, hydroxypropyl cellulose, regenerated cellulose, polyvinylpyrrolidone, poly tetrafluoroethylene, polyethylene, polypropylene, an ethylene-propylene-diene monomer (EPDM), a sulfonated EPDM, styrene-butadiene rubber, nitrile-butadiene rubber, fluorine rubber, various copolymers thereof, and the like.

**[0059]** The conductive material is a component for further improving the conductivity of a negative electrode active material, and may be added in an amount of 10 parts by weight or less, specifically 5 parts by weight, based on a total weight of 100 parts by weight of the negative electrode active material layer. The conductive material is not particularly limited as long as it has conductivity without causing a chemical change in the battery. For example, graphite such as natural graphite or artificial graphite; carbon black such as acetylene black, Ketjen black, channel black, furnace black, lamp black, and thermal black; conductive fiber such as carbon fiber and metal fiber; metal powder such as fluorocarbon powder, aluminum powder, and nickel powder; a conductive whisker such as zinc oxide and potassium titanate; a conductive metal oxide such as titanium oxide; or a conductive material such as a polyphenylene derivative, and the like may be used.

**[0060]** For example, the negative electrode active material layer may be prepared by applying a negative electrode mixture material, which is prepared by dissolving or dispersing a negative electrode active material and selectively a binder and a conductive material in a solvent, on a negative electrode current collector, followed by drying. Alternatively, the negative electrode active material layer may be prepared by casting the negative electrode mixture material on a separate support, and then laminating a film peeled off from the support on a negative electrode current collector.

**[0061]** The negative electrode active material layer may be prepared by, for example, applying a negative electrode mixture material, which is prepared by dissolving or dispersing a negative electrode active material and selectively a binder and a conductive material in a solvent, on a negative electrode current collector, followed by drying. Alternatively, the negative electrode active material layer may be prepared by casting the negative electrode mixture material on a separate support, and then laminating a film peeled off from the support on a negative electrode current collector.

**[0062]** Meanwhile, in the lithium secondary battery, a separator is to separate the negative electrode and the positive electrode and to provide a movement path for lithium ions. Any separator may be used without particular limitation as long as it is typically used as a separator in a lithium secondary battery. Particularly, a separator having high moisture-retention ability for an electrolyte as well as low resistance to the movement of electrolyte ions is preferable. Specifically, a porous polymer film, for example, a porous polymer film manufactured using a polyolefin-based polymer such as an

ethylene homopolymer, a propylene homopolymer, an ethylene/butene copolymer, an ethylene/hexene copolymer, and an ethylene/methacrylate copolymer, or a laminated structure having two or more layers thereof may be used. Also, a typical porous non-woven fabric, for example, a non-woven fabric formed of glass fiber having a high melting point, polyethylene terephthalate fiber, or the like may be used. Also, a coated separator including a ceramic component or a polymer material may be used to secure heat resistance or mechanical strength, and may be selectively used in a single-layered or a multi-layered structure.

**[0063]** In addition, the electrolyte used in the present invention may be an organic liquid electrolyte, an inorganic liquid electrolyte, a solid polymer electrolyte, a gel-type polymer electrolyte, a solid inorganic electrolyte, a molten-type inorganic electrolyte, and the like, all of which may be used in the manufacturing of a lithium secondary battery, but is not limited thereto.

**[0064]** Specifically, the electrolyte may include an organic solvent and a lithium salt.

**[0065]** Any organic solvent may be used without particular limitation as long as it may serve as a medium through which ions involved in an electrochemical reaction of a battery may move. Specifically, as the organic solvent, an ester-based solvent such as methyl acetate, ethyl acetate,  $\gamma$ -butyrolactone, and  $\epsilon$ -caprolactone; an ether-based solvent such as dibutyl ether or tetrahydrofuran; a ketone-based solvent such as cyclohexanone; an aromatic hydrocarbon-based solvent such as benzene and fluorobenzene; a carbonate-based solvent such as dimethyl carbonate (DMC), diethyl carbonate (DEC), methylethyl carbonate (MEC), ethylmethyl carbonate (EMC), ethylene carbonate (EC), and propylene carbonate (PC); an alcohol-based solvent such as ethyl alcohol and isopropyl alcohol; nitriles such as R-CN (where R is a linear, branched, or cyclic C2 to C20 hydrocarbon group and may include a double-bond aromatic ring or ether bond); amides such as dimethylformamide; dioxolanes such as 1,3-dioxolane; or sulfonates may be used. Among these solvents, a carbonate-based solvent is preferable, and a mixture of a cyclic carbonate (e.g., ethylene carbonate or propylene carbonate) having a high ionic conductivity and a high dielectric constant and a linear carbonate-based compound having a low viscosity (e.g., ethylmethyl carbonate, dimethyl carbonate, or diethyl carbonate), the mixture which may increase charging/discharging performance of a battery, is more preferable. In this case, the performance of the electrolyte solution may be excellent when the cyclic carbonate and the chain carbonate are mixed in a volume ratio of about 1:1 to about 1:9.

**[0066]** Any compound may be used as the lithium salt without particular limitation as long as it may provide lithium ions used in a lithium secondary battery. Specifically, as the lithium salt,  $\text{LiPF}_6$ ,  $\text{LiClO}_4$ ,  $\text{LiAsF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiSbF}_6$ ,  $\text{LiAlO}_4$ ,  $\text{LiAlCl}_4$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiC}_4\text{F}_9\text{SO}_3$ ,  $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_3)_2$ ,  $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ ,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ ,  $\text{LiCl}$ ,  $\text{LiI}$ ,  $\text{LiB}(\text{C}_2\text{O}_4)_2$ , or the like may be used. The lithium salt may be used in a concentration range of 0.1 M to 2.0 M. When the concentration of the lithium salt is in the above range, the electrolyte has suitable conductivity and viscosity, thereby exhibiting excellent performance, and lithium ions may effectively move.

**[0067]** In the electrolyte, in order to improve the lifespan properties of a battery, suppress the decrease in battery capacity, and improve the discharge capacity of the battery, one or more kinds of additives, for example, a halo-alkylene carbonate-based compound such as difluoroethylene carbonate, pyridine, triethylphosphite, triethanolamine, cyclic ether, ethylenediamine, n-glyme, hexaphosphoric triamide, a nitrobenzene derivative, sulfur, a quinone imine dye, N-substituted oxazolidinone, N,N-substituted imidazolidine, ethylene glycol dialkyl ether, an ammonium salt, pyrrole, 2-methoxy ethanol, or aluminum trichloride, and the like may be further included. At this time, the additive may be included in an amount of 0.1 to 5 parts by weight based on a total weight of 100 parts by weight of the electrolyte.

**[0068]** The lithium secondary battery including the positive electrode active material according to the present invention as describe above stably exhibits excellent discharging capacity, output properties, and lifespan properties, and thus, are useful for portable devices such as a mobile phone, a notebook computer, and a digital camera, and in the field of electric cars such as a hybrid electric vehicle (HEV).

**[0069]** Accordingly, according to another embodiment of the present invention, a battery module including the lithium secondary battery as a unit cell, and a battery pack including the same are provided.

**[0070]** The battery module or the battery pack may be used as a power source of one or more medium-and-large-sized devices, for example, a power tool, an electric car such as an electric vehicle (EV), a hybrid electric vehicle (HEV), and a plug-in hybrid electric vehicle (PHEV), or a power storage system.

**[0071]** The external shape of the lithium secondary battery of the present invention is not particularly limited, but may be a cylindrical shape using a can, a square shape, a pouch shape, a coin shape, or the like.

**[0072]** The lithium secondary battery according to the present invention may be used in a battery cell which is used as a power source for a small-sized device, and may also be preferably used as a unit cell for a medium- and large-sized battery module including a plurality of battery cells.

## MODE FOR CARRYING OUT THE INVENTION

**[0073]** Hereinafter, the present invention will be described in more detail with reference to embodiments. However, the embodiments according to the present invention may be modified into other various forms, and the scope of the

present invention should not be construed as being limited to the embodiments described below. The embodiments of the present invention are provided to more fully describe the present invention to those skilled in the art.

#### **Example 1**

[0074] A lithium transition metal oxide represented by  $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ , and carbon black of a hollow structure having a specific surface area of 320  $\text{m}^2/\text{g}$  and a graphitization degree ( $I_D/I_G$ ) of 1.0 were mixed such that the carbon black was 1 wt% based on 500 g of the lithium transition metal oxide. The mixture of Example 1 above was first introduced into a paint shaker (1400 Al classic shaker, Red Devil Co., Ltd) and then mixed for 60 minutes to uniformly disperse the transition metal oxide and the carbon black of a hollow structure.

[0075] The mixture above was introduced into a mechanofusion device (nobilta, Hosokawa Micron Co., Ltd) and then was treated for 10 minutes at 3,000 rpm to produce a positive electrode active material in which a carbon coating layer was formed on the lithium transition metal oxide.

#### **Example 2**

[0076] A positive electrode active material was produced in the same manner as in Example 1 except that mixing was performed such that the carbon black was 1 wt% based on 200 g of the lithium transition metal oxide.

#### **Example 3**

[0077] A positive electrode active material was produced in the same manner as in Example 1 except that mixing was performed such that the carbon black was 1 wt% based on 100g of the lithium transition metal oxide.

#### **Example 4**

[0078] A positive electrode active material was produced in the same manner as in Example 1 except that mixing was performed such that the carbon black was 1 wt% based on 50 g of the lithium transition metal oxide.

#### **Comparative Example 1**

[0079] A positive electrode active material in a form in which the lithium transition metal oxide and the carbon black were uniformly mixed was produced by introducing the mixture of Example 1 above into a paint shaker (1400 Al classic shaker, Red Devil Co., Ltd) and then mixing the same for 60 minutes.

#### **Comparative Example 2**

[0080] A lithium transition metal oxide not having a carbon coating layer formed thereon was used as a positive electrode active material.

#### **Comparative Example 3**

[0081] A lithium transition metal oxide represented by  $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ , and carbon black of a dense structure having a specific surface area of 85  $\text{m}^2/\text{g}$  and a graphitization degree ( $I_D/I_G$ ) of 1.0 were mixed such that the carbon black was 1 wt% based on 200g of the lithium transition metal oxide.

[0082] The mixture above was introduced into a mechanofusion device (nobilta, Hosokawa Micron Co., Ltd) and then was treated for 10 minutes at 3,000 rpm to produce a positive electrode active material in which a carbon coating layer was formed on the lithium transition metal oxide.

#### **Comparative Example 4**

[0083] A positive electrode active material was produced in the same manner as in Comparative Example 3 except that mixing was performed such that the carbon black was 1 wt% based on 500 g of the lithium transition metal oxide.

#### **Comparative Example 5**

[0084] The mixture of Comparative Example 3 above was introduced into a paint shaker and then mixed for 60 minutes to produce a positive electrode active material in a form in which the lithium transition metal oxide and the carbon black

were uniformly mixed.

## Experimental Example 1

### (1) Identification of surface properties of positive electrode active material

[0085] The surface properties of the positive electrode active material of each of Examples 1 and 2 and Comparative Examples 1 to 4 were confirmed and are shown in FIG. 2 to FIG. 5.

[0086] First, FIG. 2 is SEM images showing (a) the positive electrode active material of Comparative Example 2, (b) the positive electrode active material of Comparative Example 1, and (c) the positive electrode active material of Example 1. At this time, Comparative Example 2 ((a) of FIG. 2) is a positive electrode active material not having a coating layer formed on the surface thereof. Compared to (a) of FIG. 2, in the case of the positive electrode active material of Example 1, it was confirmed that a carbon-based coating layer was uniformly coated on the surface of the lithium transition metal oxide (the shape in which the surface of a particle is covered with a film of a gray shade in (c) of FIG. 2). On the other hand, in the case of the positive electrode active material produced in Comparative Example 1, it can be confirmed that residues of a carbon particle were present in the form of being adhered on the surface thereof).

[0087] FIG. 3 is SEM images showing (a) the positive electrode active material of Comparative Example 2, (b) the positive electrode active material of Comparative Example 4, and (c) the positive electrode active material of Example 1. As shown in (b) of FIG. 3, when carbon black of a dense structure was coated, it was confirmed that even when a carbon coating layer was formed in a mechanofusion manner, carbon particles were not uniformly coated on the surface of a particle, but adhered at the boundary of primary particles in an aggregated form.

[0088] FIG. 4 is SEM images showing (a) the positive electrode active material of Comparative Example 2, (b) the positive electrode active material of Example 2, and (c) the positive electrode active material of Example 1. Looking at (b) and (c) of FIG. 4, it was confirmed that carbon coating was all uniformly formed on the surface of a secondary particle and at the boundary surface between primary particles.

[0089] FIG. 5 is SEM images and energy dispersive X-ray (EDX) images of (a) the positive electrode active material of Example 2, (b) the positive electrode active material of Comparative Example 3. As shown in (a) of FIG. 5, in the case of the positive electrode active material of Example 2, when looking at the drawing on the right, it can be confirmed that carbon marked in red was uniformly applied and formed on the surface of a particle. On the other hand, looking at (b) of FIG. 5, in the case of the positive electrode active material of Comparative Example 3, it was confirmed that even when a carbon coating layer was formed by a mechanofusion method of the present invention, carbon was not uniformly applied on the surface of a particle due to the difference in carbon-based materials, and was formed by being aggregated in parts.

### (2) BET Specific surface area

[0090] The specific surface area of the positive electrode active material of each of Examples 1 to 4 and Comparative Examples 1 to 5 was measured by a BET method. Specifically, the specific surface area thereof was calculated from the adsorption amount of nitrogen gas under a liquid nitrogen temperature (77K) using Belsorp-mino II of BEL Japan Co., Ltd.

### (3) Powder electrical conductivity of positive electrode active material (S/cm)

[0091] 5 g of the positive electrode active material produced in each of Examples 1 to 4 and Comparative Examples 1 to 5 was put into a holder, and then was pressed by a force of 20 kN applied thereto. Using a 4-probe powder-only electrode (Mitsubishi Chemical, powder resistance system (MCP=PD51)), the powder electrical conductivity of each of the positive electrode active materials was measured and are shown in Table 1 below.

[Table 1]

|                       | Electrical conductivity (S/cm) | Specific surface area (m <sup>2</sup> /g) |
|-----------------------|--------------------------------|-------------------------------------------|
| Example 1             | $5.19 \times 10^{-3}$          | 1.60                                      |
| Example 2             | $4.80 \times 10^{-3}$          | 2.43                                      |
| Example 3             | $4.65 \times 10^{-3}$          | 2.85                                      |
| Example 4             | $2.97 \times 10^{-3}$          | 3.02                                      |
| Comparative Example 1 | $2.69 \times 10^{-3}$          | 3.49                                      |

(continued)

|                       | Electrical conductivity (S/cm) | Specific surface area (m <sup>2</sup> /g) |
|-----------------------|--------------------------------|-------------------------------------------|
| Comparative Example 2 | $2.17 \times 10^{-3}$          | 0.26                                      |
| Comparative Example 3 | $2.15 \times 10^{-3}$          | 1.89                                      |
| Comparative Example 4 | $2.35 \times 10^{-3}$          | 1.74                                      |
| Comparative Example 5 | $2.18 \times 10^{-3}$          | 2.25                                      |

**[0092]** As shown in Table 1 above, the positive electrode active materials produced in Examples 1 to 5 had improved positive electrode active material powder electrical conductivity compared to Comparative Examples 1 to 5.

### Experimental Example 2

**[0093]** Lithium secondary batteries were manufactured using the positive electrode active material produced in each of Examples 1 to 4 and Comparative Examples 1 to 5, and the capacity of each of the lithium secondary batteries including the positive electrode active material of each of Examples 1 to 4 and Comparative Examples 1 to 5 was evaluated.

**[0094]** Specifically, the positive electrode active material prepared in each of Examples 1 to 4 and Comparative Examples 1 and 5, a carbon black conductive material, and a PVdF binder (KF9700) were mixed at a weight ratio of 97.5:1.0:1.5 in a N-methyl-2-pyrrolidone (NMP) solvent to prepare a positive electrode slurry. The positive electrode slurry was applied on one surface of an aluminum current collector, dried at 130°C, and then roll-pressed to manufacture a positive electrode.

**[0095]** Meanwhile, artificial graphite, which was used as a negative electrode active material, a carbon black conductive material, and styrene-butadiene rubber (SBR) and carboxy methyl cellulose (CMC) as binders were mixed at a weight ratio of 96.1:0.5:2.3:1.1 in distilled water to prepare a negative electrode active material slurry. The negative electrode active material slurry was applied on a negative electrode current collector (Cu), dried, and then roll-pressed to manufacture a negative electrode.

**[0096]** A polyethylene-based separator having a thickness of 15  $\mu\text{m}$  was interposed between the positive electrode and the negative electrode manufactured above to manufacture an electrode assembly, and the electrode assembly was placed inside a battery case. Thereafter, an electrolyte solution was injected into the inside of the case to manufacture a lithium secondary battery. At this time, as the electrolyte solution, an electrolyte solution prepared by dissolving 1 M of  $\text{LiPF}_6$  in a mixed organic solvent in which ethylene carbonate (EC) and ethyl methyl carbonate (EMC) were mixed in a volume ratio of 1:2 was used to manufacture a lithium secondary battery according to each of Examples 1 to 4 and Comparative Examples 1 to 5.

**[0097]** Next, each of the lithium secondary batteries manufactured in Examples 1 to 4 and Comparative Examples 1 to 5 was charged to 4.25 V with a constant current of 0.2 C at 45°C with a cut-off of 0.05 C. Next, each of the lithium secondary batteries was discharged to 2.5 V with a constant current of 0.2 C to measure initial charge and discharge capacities.

**[0098]** Thereafter, charging was performed with a 0.2 C constant current to 4.25 V with a 0.05 C cut off, and then discharging was performed with a 2.0 C constant current until 2.5 V was reached. The above charge/discharge behavior was set as one cycle, and the cycle was repeated 2 times. Thereafter, the discharge capacity properties at 2.0 C with respect to 0.2 C discharge capacity of each of the lithium secondary batteries according to Examples 1 to 4 and Comparative Examples 1 to 5 were measured and are shown in Table 2 below.

[Table 2]

|                       | 2.0 C discharge capacity ratio(% , with respect to 0.2 C discharge capacity) |
|-----------------------|------------------------------------------------------------------------------|
| Example 1             | 90.3                                                                         |
| Example 2             | 88.1                                                                         |
| Example 3             | 86.5                                                                         |
| Example 4             | 79.9                                                                         |
| Comparative Example 1 | 78.7                                                                         |
| Comparative Example 2 | 75.5                                                                         |
| Comparative Example 3 | 74.9                                                                         |

(continued)

|                       |                                                                              |
|-----------------------|------------------------------------------------------------------------------|
|                       | 2.0 C discharge capacity ratio(% , with respect to 0.2 C discharge capacity) |
| Comparative Example 4 | 73.6                                                                         |
| Comparative Example 5 | 75.3                                                                         |

**[0099]** As shown in Table 2 above, it was confirmed that the capacity properties of the secondary batteries of Examples 1 to 4 were superior to those of the secondary batteries of Comparative Examples 1 to 5.

## Claims

1. A method for producing a positive electrode active material, the method comprising:

preparing a lithium transition metal oxide in a form of a secondary particle in which primary particles are aggregated;  
mixing the lithium transition metal oxide and a carbon-based material of a hollow structure having a plurality of pores to form a mixture; and  
surface treating the mixture in a mechanical manner to form a carbon coating layer on the surface of the lithium transition metal oxide,  
wherein the carbon-based material of a hollow structure having a plurality of pores has a specific surface area of 200 m<sup>2</sup>/g or greater and a graphitization degree( $I_D/I_G$ ) of 0.5 or greater.

2. The method of claim 1, wherein the carbon-based material is mixed in an amount of 0.1 to 2 parts by weight based on 100 parts by weight of the lithium transition metal oxide.

3. The method of claim 1, wherein the surface treating of the mixture in a mechanical manner is performed by a mechanofusion method.

4. The method of claim 1, wherein the carbon-based material has a specific surface area of from 200 m<sup>2</sup>/g to less than 500 m<sup>2</sup>/g.

5. The method of claim 1, wherein the carbon-based material has a graphitization degree ( $I_D/I_G$ ) of from 0.5 to 2.0.

6. A positive electrode active material comprising:

a lithium transition metal oxide in the form of a secondary particle in which primary particles are aggregated; and  
a carbon coating layer formed on the surface of the lithium transition metal oxide, wherein the carbon coating layer is formed on a surface of the primary particle and a surface of the secondary particle of the lithium transition metal oxide, and wherein the positive electrode active material has a BET specific surface area of 10 m<sup>2</sup>/g or less.

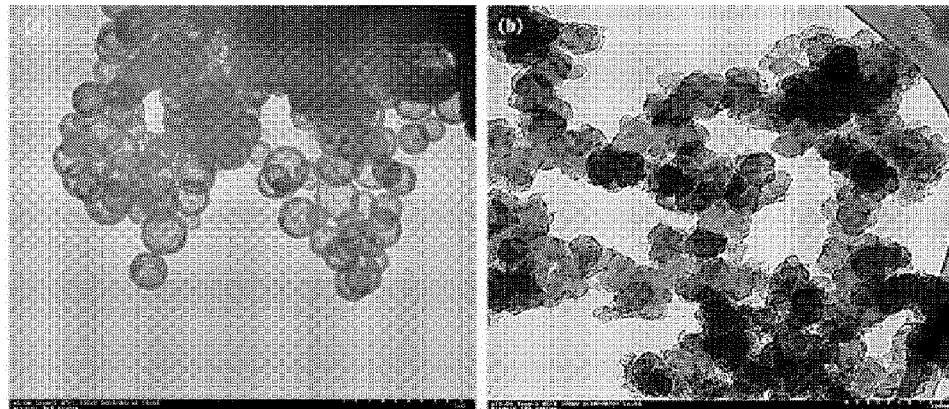
7. The positive electrode active material of claim 6, wherein the positive electrode active material has a BET specific surface area of 1.0 m<sup>2</sup>/g to 10.0 m<sup>2</sup>/g.

8. The positive electrode active material of claim 6, wherein the positive electrode active material has a powder electrical conductivity of  $2.7 \times 10^{-3}$  S/cm to  $10.0 \times 10^{-3}$  S/cm, which is measured after pressing the positive electrode active material by applying a force of 5 to 20 kN thereto.

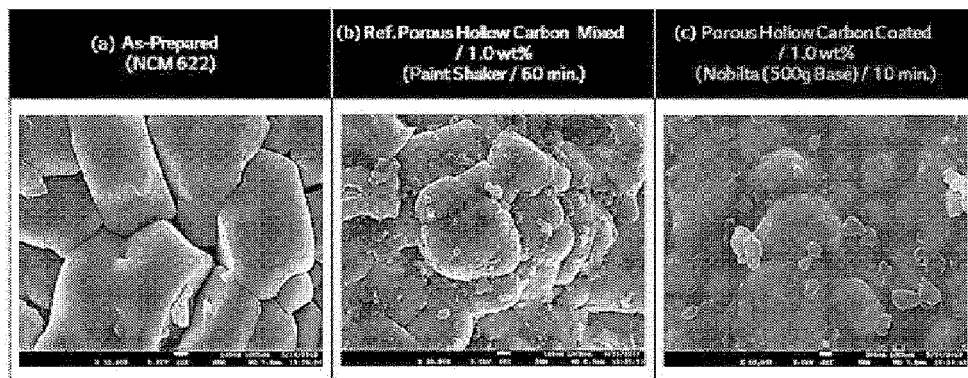
9. A positive electrode for a lithium secondary battery comprising the positive electrode active material of claim 6.

10. A lithium secondary battery comprising the positive electrode for a lithium secondary battery according to claim 9.

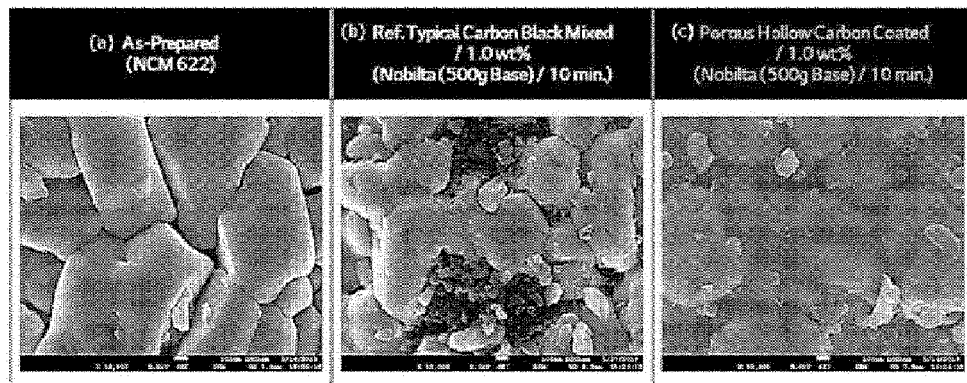
[FIG. 1]



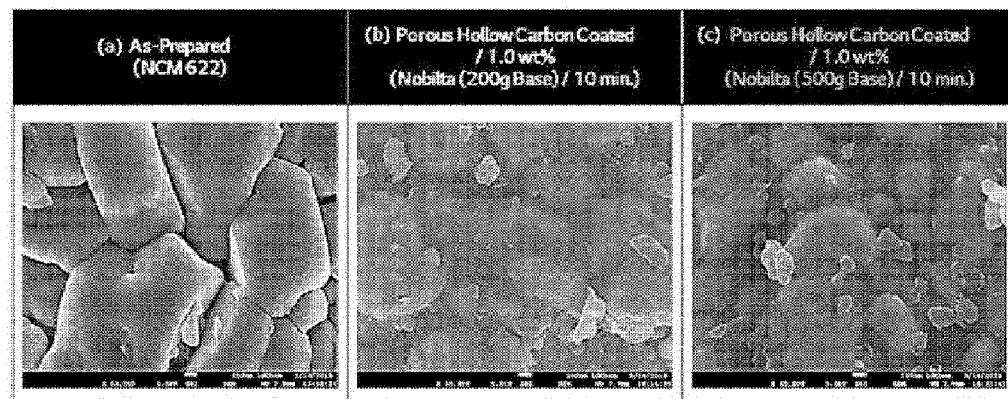
[FIG. 2]



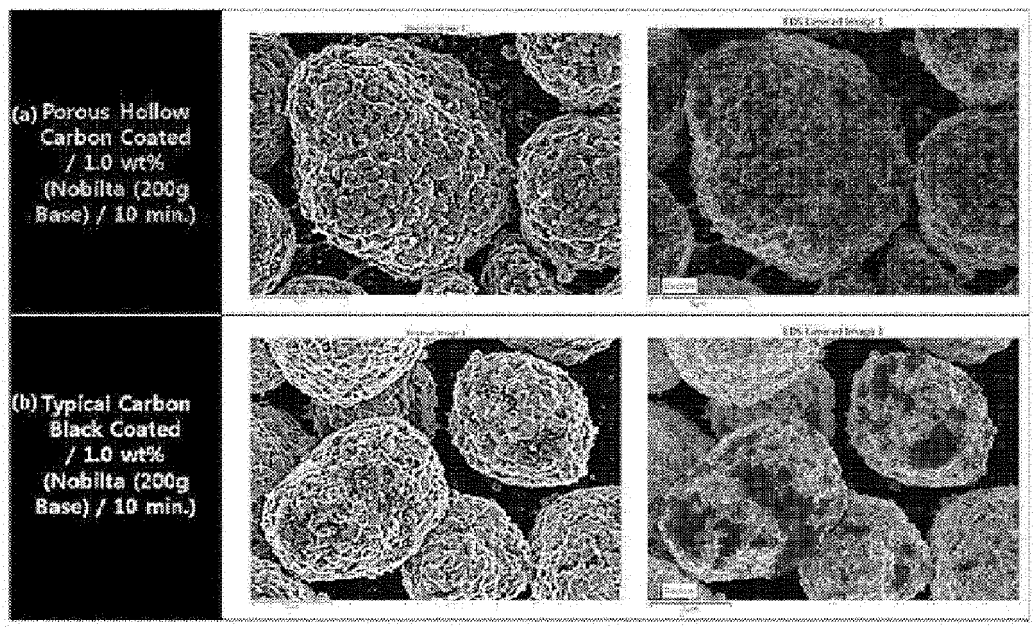
[FIG. 3]



[FIG. 4]



[FIG. 5]



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2020/013953

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|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>A. CLASSIFICATION OF SUBJECT MATTER</b><br><b>H01M 4/36(2006.01)i; H01M 4/62(2006.01)i; H01M 4/525(2010.01)i; H01M 4/505(2010.01)i; H01M 10/052(2010.01)i; C01G 53/00(2006.01)i</b><br><br>According to International Patent Classification (IPC) or to both national classification and IPC                                                                                                                                                                                                                                                                                                                                                                                                | <b>B. FIELDS SEARCHED</b><br><br>Minimum documentation searched (classification system followed by classification symbols)<br>H01M 4/36(2006.01); C01B 25/32(2006.01); H01M 12/08(2006.01); H01M 4/02(2006.01); H01M 4/04(2006.01); H01M 4/13(2010.01); H01M 4/38(2006.01); H01M 4/583(2010.01); H01M 4/96(2006.01)<br><br>Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched<br>Korean utility models and applications for utility models: IPC as above<br>Japanese utility models and applications for utility models: IPC as above<br><br>Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)<br>eKOMPASS (KIPO internal) & keywords: 리튬(lithium), 전이금속(transition metal), 중공(hollow), 탄소(carbon), 코팅(coating), 메카노퓨전(mechanofusion) |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |
| <b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |
| Category*                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | Relevant to claim No.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |
| Y                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | KR 10-2013-0109785 A (SAMSUNG SDI CO., LTD.) 08 October 2013 (2013-10-08)<br>See claims 1, 14, 16, 17, 19 and 20; and paragraphs [0027], [0032] and [0077].                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | 1-10                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |
| Y                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | JP 2019-149356 A (SUMITOMO OSAKA CEMENT CO., LTD.) 05 September 2019 (2019-09-05)<br>See claims 1 and 8; and paragraphs [0041] and [0043].                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | 1-10                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | JP 2013-131325 A (SONY CORP.) 04 July 2013 (2013-07-04)<br>See claims 1 and 2.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | 1-10                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | JP 2018-056126 A (SAMSUNG ELECTRONICS CO., LTD. et al.) 05 April 2018 (2018-04-05)<br>See claim 1.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | 1-10                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | JP 09-092265 A (DENSO CORP.) 04 April 1997 (1997-04-04)<br>See claims 1 and 2.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | 1-10                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |
| <input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |
| * Special categories of cited documents:<br>"A" document defining the general state of the art which is not considered to be of particular relevance<br>"D" document cited by the applicant in the international application<br>"E" earlier application or patent but published on or after the international filing date<br>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)<br>"O" document referring to an oral disclosure, use, exhibition or other means<br>"P" document published prior to the international filing date but later than the priority date claimed |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             | "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention<br>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone<br>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art<br>"&" document member of the same patent family |
| Date of the actual completion of the international search<br><b>15 January 2021</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             | Date of mailing of the international search report<br><b>18 January 2021</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |
| Name and mailing address of the ISA/KR<br><b>Korean Intellectual Property Office<br/>         Government Complex-Daejeon Building 4, 189 Cheongsaro, Seo-gu, Daejeon 35208</b><br>Facsimile No. +82-42-481-8578                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             | Authorized officer<br><br><br>Telephone No.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |

Form PCT/ISA/210 (second sheet) (July 2019)

**INTERNATIONAL SEARCH REPORT**  
**Information on patent family members**

International application No.

**PCT/KR2020/013953**

| Patent document<br>cited in search report | Publication date<br>(day/month/year) | Patent family member(s) | Publication date<br>(day/month/year) |
|-------------------------------------------|--------------------------------------|-------------------------|--------------------------------------|
| KR 10-2013-0109785 A                      | 08 October 2013                      | EP 2645455 A1           | 02 October 2013                      |
|                                           |                                      | US 2013-0260252 A1      | 03 October 2013                      |
| JP 2019-149356 A                          | 05 September 2019                    | JP 6501011 B1           | 17 April 2019                        |
| JP 2013-131325 A                          | 04 July 2013                         | CN 103988347 A          | 13 August 2014                       |
|                                           |                                      | CN 103988347 B          | 09 June 2017                         |
|                                           |                                      | EP 2797144 A1           | 29 October 2014                      |
|                                           |                                      | EP 2797144 B1           | 15 February 2017                     |
|                                           |                                      | JP 5982811 B2           | 31 August 2016                       |
|                                           |                                      | KR 10-1950544 B1        | 20 February 2019                     |
|                                           |                                      | KR 10-2014-0105460 A    | 01 September 2014                    |
|                                           |                                      | US 2014-0349187 A1      | 27 November 2014                     |
|                                           |                                      | WO 2013-094404 A1       | 27 June 2013                         |
| JP 2018-056126 A                          | 05 April 2018                        | CN 107871877 A          | 03 April 2018                        |
|                                           |                                      | KR 10-2018-0034211 A    | 04 April 2018                        |
|                                           |                                      | US 2018-0090802 A1      | 29 March 2018                        |
| JP 09-092265 A                            | 04 April 1997                        | JP 3601124 B2           | 15 December 2004                     |
|                                           |                                      | US 5789114 A            | 04 August 1998                       |

Form PCT/ISA/210 (patent family annex) (July 2019)

**REFERENCES CITED IN THE DESCRIPTION**

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**Patent documents cited in the description**

- KR 1020190127314 [0001]